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High temperature latent heat thermal energy storage: Phase change materials, design considerations and performance enhancement techniques

Bruno Cárdenas*, Noel León[1]

CIDYT, Monterrey Institute of Technology, Ave. Eugenio Garza Sada 2501 South, Col. Tecnológico, 64849, Monterrey, Nuevo León, México

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A B S T R A C T

A very common problem in solar power generation plants and various other industrial processes is the existing gap between the period of thermal energy availability and its period of usage. This situation creates the need for an effective method by which excess heat can be stored for later use. Latent heat thermal energy storage is one of the most efficient ways of storing thermal energy through which the disparity between energy production or availability and consumption can be corrected, thus avoiding wastage and increasing the process efficiency.

This paper reviews a series of phase change materials, mainly inorganic salt compositions and metallic alloys, which could potentially be used as storage media in a high temperature (above 300 °C) latent heat storage system, seeking to serve the reader as a comprehensive thermophysical properties database to facilitate the material selection task for high temperature applications.

Widespread utilization of latent heat storage systems has been held back by the poor thermal conductivity and some other inherent drawbacks of the use of PCMs; this paper reviews several heat transfer and performance enhancement techniques proposed in the literature and discusses a number of design considerations that must be taken into account aiming to provide a broad overview for the design of high temperature latent heat based thermal energy storage systems.

Contents

* Corresponding author. Tel.: +52 81 8358 2000, mobile: +52 81 1066 0171.
E-mail addresses: b.cardenas.phd.mty@itesm.mx, brunoz8@hotmail.com (B. Cárdenas), noel.leon@itesm.mx (N. León).
[1] Tel.: +52 81 1269 2355.

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1. Introduction

Thermal energy storage (TES) is of great importance to many fields of engineering since it offers numerous benefits for various areas of the industry. For instance, one of the most common problems that solar power generation systems face is the gap that exists between the availability of the solar resource and energy demand, causing the need for an effective method by which excess heat collected during periods of high solar irradiation can be stored and retrieved later for use at night or during periods of darkness [1]. In addition to correcting the disparity between energy production or availability and consumption, thermal energy storage increases the effective use of equipment whose operation requires a heat supply [2].

A similar problem occurs in several industrial processes, where a great amount of waste heat could be reused by means of a waste heat recovery system; however in many cases the heat availability period differs from its usage period, and not having a storage system means all that excess energy, unusable at the moment of generation, will be simply wasted.

TES systems can help to reduce backup equipment required to secure power supply in hospitals, computer centers, and all those places where a reliable supply is vital [3] also, thermal energy storage can be used to provide thermal comfort in many types of buildings with heavy heating and air conditioning needs and thereby achieve a reduction in electric rates [1].

2. Thermal energy storage methods

There are three methods for storing thermal energy storage, the first two being the most widely used in TES systems:

- sensible heat storage;
- latent heat storage;
- thermochemical storage.

The present review article focuses mainly on latent heat storage with a transition from solid to liquid phase for reasons explained further on.

2.1. Sensible heat storage

Sensible heat storage (SHS) involves heating a material, without actually causing a phase change in it. Thermal energy is accumulated as a result of increasing the temperature of the storage medium. The amount of energy stored depends on the specific heat, the temperature change and the amount of material [4] and may be represented by the following expression:

$$Q = \int_{T_i}^{T_f} mC_p dT = mC_{ap}(T_f - T_i) \tag{1}$$

SHS systems can be classified on the basis of storage material as liquid media sensible storage (such as water, oil, molten salt, etc.) or solid media sensible storage (such as rocks, and metals).

2.2. Latent heat storage

Latent heat thermal energy storage (LHS) involves heating a material until it experiences a phase change, which can be from solid to liquid or from liquid to gas; when the material reaches its phase change temperature it absorbs a large amount of heat in order to carry out the transformation, known as the latent heat of fusion or vaporization depending on the case, and in this manner the energy is stored.

The following graph further explains the storage mechanism; as a solid material is heated its temperature begins to increase in direct proportion to the received energy until it reaches the melting temperature. Beyond this point, the energy delivered to the material ceases to raise the temperature, and is used instead to perform the transition from solid to liquid (latent heat), that is, the material stores isothermally the thermal energy received; once the transformation is complete and the material is wholly in the liquid state, the temperature begins to increase again as it receives a heat input until it reaches the vaporization point where the occurred in the first phase change is repeated. The heating process works the same way for cooling, which means that it is possible to extract the stored energy as latent heat at a constant temperature (Fig. 1).

As can be seen it is impossible to exclusively store latent heat, as to reach the phase change point the material had to undergo a temperature increase which represents storage of sensible heat. The storage capacity of an LHS system can be represented by the following expression [4]:

$$Q = \int_{T_i}^{T_m} mC_p dT + m a_m \Delta h_m + \int_{T_m}^{T_f} mC_p dT \tag{2}$$

$$Q = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)] \tag{3}$$

The first term of the equation represents the sensible heat stored by the material temperature increase from its initial temperature to the phase change temperature, the second term represents the energy stored by the latent heat of the material during the phase change, the amount of energy stored depends on the amount of material, the specific latent heat and the fraction of the material

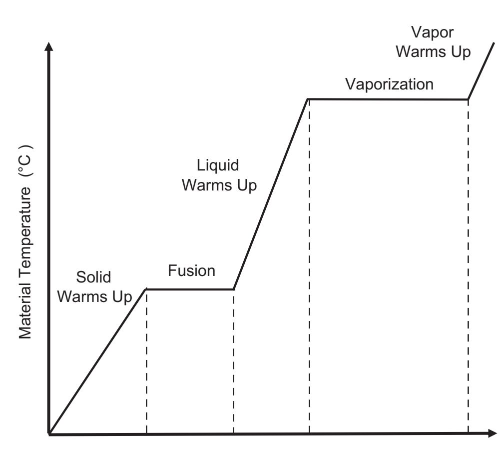


Fig. 1. Temperature increase profile in respect of supplied heat.

that has experienced a transformation. If the material is further heated after the phase change a third term appears in the equation to account again for sensible heat storage.

Materials used for latent heat thermal energy storage are known as phase change materials (PCMs). The PCM may undergo solid–solid, solid–liquid and liquid–gas phase transformations.

2.2.1. Solid–solid latent heat storage

Generally, LHS systems use the latent heat between solid and liquid phases of the storage medium, whereby the PCM is required to be contained or encapsulated within a container to prevent the liquid from leaking; however, the capsules decrease the energy density of the system and increase the cost of production. To overcome these problems the use of the solid–solid phase change of certain materials has been proposed as an alternative (SSPCM). Relatively few SSPCM with suitable transition temperatures and latent heats for thermal storage applications have been identified.

Solid–solid phase change is quite simple and provides advantages such as easy handling and cost effectiveness, because as it has been said, the lack of liquid material eliminates the risk of leakage and hence there is no need for encapsulation. There has been work focused on developing steel alloy based SSPCM for high temperature waste heat recovery [5].

Despite the advantages that SSPCM offer, their latent heat of transition is about one order of magnitude smaller than that of the solid–liquid PCM, which is a major drawback that has to be addressed in order to achieve a greater introduction of this technology. SSPCM metal alloys are expected to be used in the future in stationary systems, as structural materials with a heat storage function, because they have a small latent heat per mass unit, but a rather large per volume unit. This means that they are suitable for energy storage on site but unsuitable for energy transport.

2.2.2. Liquid–gas latent heat storage

Transformations from liquid to gas have the highest latent heat of phase change; however, the enormous changes in the volume of the storage material associated with the evaporation make the storage complex and highly impractical; thus the possible use for TES systems is discarded, the reason why the gaseous state information of many materials is quite limited.

2.2.3. Solid–liquid latent heat storage

The change from solid to liquid phase is the transformation that has been most widely studied and used in LHS applications; despite having a smaller latent heat compared with the liquid–gas phase change it does not present such a serious problem regarding volumetric expansion, which is generally in the order of an increase of 10% or less relative to the original volume [6].

During fusion, the heat is transferred to the PCM in the first instance by conduction and by natural convection afterwards; this is because the solid region moves away from the heat transfer surface and the liquid region thickness increases near the heat transfer surface. Since the liquid PCM thermal conductivity is lower than that of the solid PCM, the conductive heat transfer becomes almost negligible as the melting process continues due to the density gradient that exists in the liquid PCM.

Contrary to the melt, solidification is dominated by conduction; during solidification natural convection exists only in the beginning of the process and as time passes the effect is negligible compared to the conduction effect [7].

Using solid–liquid transition PCMs has a number of technical complications; one of the biggest problems that has contributed to the widespread use of LHS remains unsatisfactory so far is the unacceptably low thermal conductivity of the PCMs; besides that, there are other problems such as the complexity of the container, phase segregation and subcooling, which can be very severe and completely impede the extraction of the stored energy [8].

To avoid these problems, various techniques for improving the heat transfer in fusion LHS systems have been proposed, and such methods will be later explained in detail.

The distinctive feature and main advantage of LHS systems is the isothermal operation at the phase change temperature of the material, i.e. it is able to deliver the stored energy at a nearly constant temperature. Another advantage offered by this type of storage is its compactness; due to that in most materials the latent heat of fusion is much greater than the specific heat. For example, 80 times more energy is required to melt 1 g of ice (latent heat) than to raise the temperature of 1 g of water 1 °C (sensible heat).

Given its characteristics, the phase change materials are chosen over sensible heat materials primarily for applications where volume and weight are restrictions and therefore a high energy density is required or when there is a load whose power input must be at constant temperature.

Typically, PCMs are placed in long slender tubes tightly packed within a container. During a storage cycle in a solar application, for example, the heat collected by the unit is transported by a heat transfer fluid (HTF) through the narrow spaces between the tubes, melting the PCM. During the extraction cycle or heat recovery, the circulation of low temperature HTF collects the energy stored in the PCM and transports it to the thermal load.

Any LHS system must possess at least the three following basic components:

- a substance or energy storage medium, which undergoes a solid to liquid phase change at the required temperature range where most of the added heat is stored as latent heat;
- a container for containing the storage medium;
- a heat exchange surface to transfer the energy from the heat source to the PCM and from the PCM to the load [9,10].

2.3. Thermochemical heat storage

There is a third method of thermal energy storage which consists in the use of reversible endothermic chemical reactions. The chemical heat is the heat necessary to dissociate or break joints in a chemical compound; nearly all of this energy will be retrieved later when a synthesis reaction takes place. This type of storage offers very attractive advantages; however, the development of reversible thermochemical reactions is at a very early stage [11].

3. Phase change materials

3.1. Suitable material selection

The selection of the PCM to be used in a LHS as the storage media is directed by a series of desirable properties, proposed by Abhat [12] and Lane [4] and several other researchers [3,6,8,12–20] considering thermodynamic, physical, chemical and economic aspects.

When selecting a PCM for a particular application, the phase change temperature of the material must be equal or very similar to the operating temperature. The latent heat should be as high as possible, especially on a volumetric basis to minimize the size of the storage unit. In addition to that, a high specific heat is wanted for providing additional sensible storage capacity. A high thermal conductivity, in both states, solid and liquid, is desirable to improve the energy storage and extraction processes, and to obtain a more uniform temperature distribution within the storage unit.

A high density, small volume changes between solid and liquid phases and low vapor pressure at the operating temperature are sought to maintain a small size storage unit and a simple design of container. The PCM must exhibit congruent melting, otherwise there will be irreversible component segregation and the storage capacity will be gradually lost with work cycles. An important aspect of the material is for to it to have null or insignificant subcooling and a sufficient crystallization rate; this has been one of the most problematic aspects of PCM development. A subcooling of more than a few degrees will interfere with heat extraction and may completely impede it.

It is important that the selected PCM is chemically stable to provide a reasonable lifetime of the storage unit, given that during operation it may undergo oxidative degradation, chemical decomposition or incompatibility with the container materials. Also, for safety reasons, the PCM should not be toxic, flammable, or explosive.

Finally, it is important to consider the economic aspect; the PCM must be abundant and commercially available, and have a reasonable cost for the application that allows development to be feasible.

3.2. PCM classification

A number of phase change materials are available for a wide range of operating temperatures. In 1983, Abhat published a paper on latent heat TES in which a classification of materials, still widely used today by various researchers, was presented.

As it can be seen in the classification diagram, there are organic and inorganic materials which can be used as LHS media. Organic materials include paraffins and non-paraffins such as fatty acids, while inorganic materials comprise salt hydrates, saline composites and metallic alloys (Fig. 2). In general, inorganic compounds have near twice the energy storage capacity per volume unit than organic compounds and they possess much higher operating temperatures.

Despite the large amount of materials identified as suitable PCMs from a melting point and latent heat standpoint, it is impossible to find a PCM that satisfies all required criteria for being a suitable storage medium; therefore engineers and developers must compensate poor physical properties with an appropriate system design; for example, metallic fins can be employed to increase the thermal conductivity of the PCM and subcooling can be suppressed by adding nucleating agents into the storage media.

3.3. High temperature phase change materials

High temperature PCMs with melting temperatures above 300 °C, which for their melting point and storage capabilities have the potential for being used as storage media in solar power plants or industrial waste heat recovery systems, are reviewed. This high temperature group includes inorganic salts, salt eutectic compounds, metal alloys and metallic eutectics. Materials in the range of 300–550 °C are compatible with the currently available heat transfer technology in solar plants; however alternative heat transfer fluids such as supercritical CO_2 and other molten salts are under investigation by research teams worldwide; therefore, higher operation temperatures are going to be achievable and higher storage temperatures (above 550 °C) will be required [21].

3.3.1. Inorganic salts and saline compounds

In the considered temperature range, above 300 °C, inorganic salts are of great interest. Tables 1 and 2 present pure inorganic salts, and saline compounds that have been investigated by several researchers for their potential for being used as PCM in high temperature applications. Some of their thermophysical properties are included, such as melting temperature, latent heat of fusion and density in solid state and in some cases in both, solid and liquid states.

High heat of fusion of chlorides and fluorides, and the low cost of the former have encouraged further studies of salt compositions on their basis. Eutectic compositions on the basis of fluorides and chlorides which have been proposed by authors as potential PCMS are presented in Table 3, and salt compositions based on nitrates, carbonates, hydroxides and other salts, besides fluorides and chlorides are also of considerable interest.

3.3.2. Metals and metal alloys

Metallic materials have not been seriously considered as PCM for LHS systems for their elevated weight; however, when volume is a priority they are good candidates, capable of competing with salts due to the high latent heat of fusion per volume unit they possess.

It is known that salts have a set of disadvantages that limit their application; among them is the very low thermal conductivity, corrosivity, non-negligible phase change associated volume increase and considerable subcooling. Metallic materials are generally exempt of said problems, so despite their low stored energy rate by mass unit, in comparison with salts, they are an interesting alternative.

It is possible to mention, as the most notable characteristics of this group of materials, their high thermal conductivity, which eliminates the need of adding additional structures within the container for heat conduction improvement, their high heat of

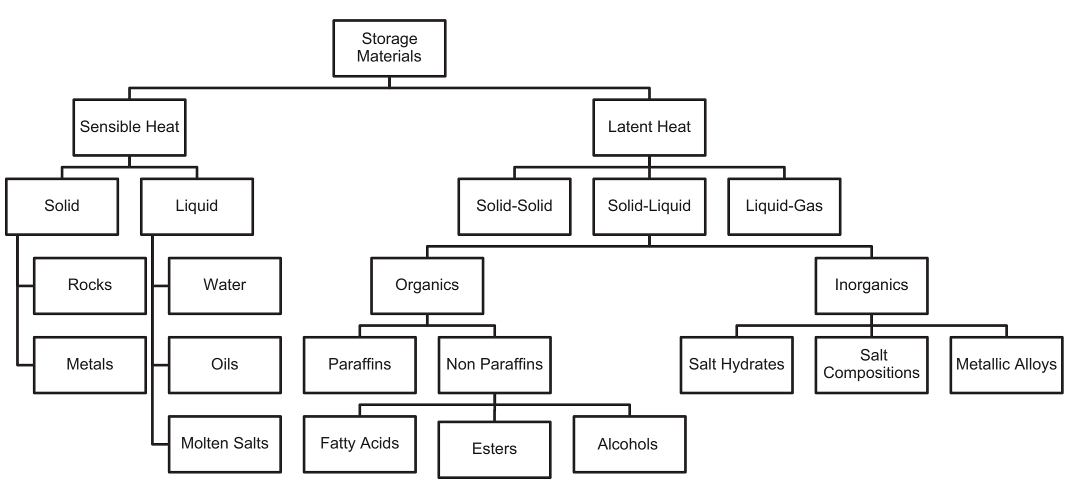


Fig. 2. PCM classification diagram.

Table 1
Thermophysical properties of some inorganic salts with PCM potential.

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (g/cm^3)		Reference
			Solid	Liquid	
$NaNO_3$	306	182	2.26	1.908	[2,3,22–26]
$RbNO_3$	312	31	3.685	2.82	[22]
NaOH	323	170	2.13	n.a	[21]
KNO_3	334	266	2.109 @16 °C	n.a	[1,3,21,23,24,26]
KOH	380	149.7	2.044	1.47	[3,21,23,26]
$CsNO_3$	409	71	2.5	n.a	[22]
AgBr	432	48.8	1.1	n.a	
LiI	458	109	3.49	3.109	[22]
LiOH	462	873	1.46	n.a	
$PbCl_2$	501	78.7	5.6	n.a	
SrI_2	527	57	4.55	4.085	[22]
LiBr	550	203	3.46	2.528	[22]
$Ca(NO_3)_2$	560	145	2.113	n.a	[21,22]
$Ba(NO_3)_2$	594	209	3.23	n.a	[22]
$Sr(NO_3)_2$	608	221	2.11	n.a	[22]
LiCl	610	441	2.07	1.502	[22]
CsI	629	96	4.51	3.197	[22]
MgI_2	633	93	4.43	3.05	[22]
CsBr	638	105	4.44	3.133	[22]
CsCl	645	121	3.7808	2.79	[22]
RbI	646	104	3.55	2.904	[22]
$SrBr_2$	650	41	4.175	3.7	[22]
NaI	661	158	3.67	n.a	[22]
$FeCl_2$	677	337.9	3.16	n.a	
KI	681	145	3.12	n.a	[22]
Na_2MoO_4	688	109	3.78	n.a	[22]
LiH	688	2678	0.82	0.58	[27]
RbBr	692	141	3.35	2.715	[22]
CsF	693	143	4.115	3.649	[22]
Na_2WO_4	696	107	3.12	n.a	[22]
Li_2MoO_4	703	281	3.78	n.a	[22]
$MgBr_2$	711	214	3.72	2.62	[22]
$MgCl_2$	714	454	2.32	1.68	[3,21,22,25,26]
RbCl	719	198	2.8	2.248	[22]
BaI_2	726	68	5.15	4.26	[22]
Li_2CO_3	732	509	2.11	n.a	
KBr	734	215	2.75	2.127	[22]
$CaBr_2$	736	145	3.35	n.a	[22]
Li_2WO_4	740	157	4.179	n.a	[22]
NaBr	749	255	3.2	2.342	[22]
KCl	771	353	1.98	1.527	[21,22]
$CaCl_2$	772	253	2.15	2.085	[22]
RbF	774	248	3.557	2.87	[22]
CaI_2	783	142	3.956	3.443	[22]
Na_2CrO_4	794	146	2.73	n.a	[22]
NaCl	802	482	2.16	1.556	[3,21–23,25,26]
PbF_2	824	60	8.445	n.a	
LiF	845	1044	2.64	1.81	[22,28]
$LiBO_2$	845	504.7	2.223	n.a	
Na_2CO_3	854	275.7	2.533	1.972	[3,21,23,26,29]
$BaBr_2$	857	108	4.78	3.991	[22]
KF	858	468	2.37	1.91	[3,22,25,26,29]
Li_2SO_4	858	84	2.22	2.003	[22]
ZnF_2	872	400	4.95	n.a	
$SrCl_2$	875	103	3.0	2.727	[22]
Na_2SO_4	884	165	2.68	n.a	[21,22]
K_2CO_3	897	235.8	2.29	n.a	[2,3,21,26]
K_2WO_4	923	86	3.12	n.a	[22]
$BaCl_2$	961	76	3.856	3.174	[22]
K_2CrO_4	973	170	2.66	n.a	[22]
NaF	996	794	2.558	1.948	[22]
$PbSO_4$	1000	133	6.2	n.a	
Cs_2SO_4	1015	101	4.243	3.1	[22]
K_2SO_4	1069	212	2.66	n.a	[22]
Rb_2SO_4	1070	145	3.613	n.a	[22]
Na_2SiO_3	1088	424	1.749	n.a	
$MgSO_4$	1130	122	2.66	n.a	[22]
Cu_2S	1130	60.44	6.473	n.a	
FeS	1195	358	4.84	n.a	
MgF_2	1263	938	3.15	n.a	[22]
BaF_2	1320	119	4.89	4.14	[22]
$CaCO_3$	1330	142	2.93	n.a	
CaF_2	1418	391	3.18	2.52	[22]

Table 1 (*continued*)

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (g/cm^3)		Reference
			Solid	Liquid	
SrF_2	1440	231	4.24	3.47	[22]
$CaSO_4$	1460	203	2.32	n.a	[22]
$BaSO_4$	1512	188	4.5	n.a	[22]
$BaCO_3$	1555	200	3.89	n.a	
$SrSO_4$	1605	196	3.96	n.a	[22]

fusion per volume unit, low specific heat and relatively low vapor pressure [6].

Among the first authors to analyze the possibility of storing thermal energy using the latent heat of fusion of metals and report the thermal properties of metallic alloys studied are Birchenal and Telkes [71], Farkas and Birchenall [69] and Gasanaliev and Gamataeva [68].

Tables 4 and 5 list the metals and metal alloys with melting temperatures above 300 °C proposed and studied by various researchers as possible high temperature PCMs.

Zalba et al. [3] and other researchers note in their work that the thermophysical properties of the PCM have not been studied enough yet to have clear recommendations for the design of a commercial LHS unit and so far there is no comprehensive database of thermophysical properties which facilitates the selection of materials.

The authors point out that there are major discrepancies between the data of melting temperature, latent heat of fusion, thermal conductivity and density in both solid and liquid, for the same PCM. This inconsistency in the information is largely due to the fact there are no national or international standard methods to test the PCM, the lack of which makes comparisons difficult when evaluating the PCM convenience for a particular application. A standard platform should be developed to ensure that in the various PCM experiments carried out, the same test procedure and analysis are applied, to allow subsequent comparison and such that gained knowledge from a particular test can be applied to others [72].

When analyzing their publications it also becomes apparent that, practically all experiments for properties determination of possible PCMs have been limited only to temperature and latent heat of fusion measurements and except very few cases there are no measurements done to establish the temperature dependence of certain parameters such as thermal conductivity, heat capacity and density of the PCM prospects [73].

3.4. Design considerations and problems related to PCM usage

PCMs offer great benefits; nonetheless they present different problems and technical difficulties that have limited its widespread use in practical applications. Among the most important issues to be resolved is the type of vessel required to contain the PCM and how to ensure its long-term stability, i.e. the number of cycles that both components can withstand without degradation of their properties. The long-term stability of the system can be compromised by two factors, poor stability of the properties of materials under extensive thermal cycling and/or corrosion and chemical incompatibility between the PCM and its container [3].

Some authors have focused their work on characterizing the physical and thermal stabilities of various PCMs and their containers, with the purpose of determining if repeated thermal cycling affects the thermal properties of the system and its long-term stability [74,75]. There are some other drawbacks as well, solid deposits on the heat transfer surfaces, phase segregation and subcooling and the very low thermal conductivity of the PCMs available, which is one of the major problems that researchers face and has contributed to the fact that, as already mentioned, the large-scale use of LHS remains unsatisfactory so far [76].

Many PCMs, especially salt hydrates, do not solidify immediately upon being cooled below its melting temperature, but crystallization starts at a temperature considerably lower than the phase change temperature, and this effect is known as subcooling [77]. The presence of this condition reduces the usefulness of the material and in severe cases, when there is no nucleation, it can completely prevent the extraction of the stored energy. The use of nucleating agents, containers with rough inner walls and the cold finger technique have been proposed to eliminate subcooling [4,78–80].

Another problem associated with the saline compounds, and present in other materials, is phase segregation, which causes the process to become irreversible and leads to a continuous decline in the storage efficiency. In an effort to overcome these problems, several researchers have resorted to heat transfer by direct contact between an immiscible HTF and the PCM, and the agitation caused by the HTF helps minimize the subcooling and prevents phase segregation [81–85]. Furthermore, various techniques such as the use of thickening and nucleating agents, rotative devices [4,86] and encapsulation in metal and plastic matrices have been extensively tested to prevent phase separation and the incorrect re-solidification that it entails.

4. Heat transfer and performance enhancement techniques

4.1. Fins and extended surfaces

In order to provide additional heat transfer surface in LHS systems and contribute to the improvement of performance, the use of extended surfaces or fins has been proposed. In LHS the role played by different configurations of fins on performance improvement has been extensively studied by many researchers.

The extension of the heat transfer surface using capsules or finned tubes will reduce the distance for the transport of thermal energy into the PCM, thereby improving heat transfer. Normally encapsulation is used for low temperature materials such as paraffins, although it is possible to encapsulate PCM with melting temperatures above 200 °C; however the required material to do so is generally expensive. When using a rigid capsule for containing PCM, the initial volume of material should not exceed 80% of the total volume of the capsule, so that it can withstand the pressure exerted by the variation of the density of the PCM during work cycles [87].

Another design generally used to improve heat transfer in high temperature LHS units consists of fins arranged orthogonally to the axis of the pipes of the heat transfer fluid. The material of the fins may be graphite foil, aluminum, steel or copper. Due to the advantages of the graphite foil, such as high thermal conductivity, low density and good corrosion resistance against nitrate salts and nitrite at high

Table 2
Thermophysical properties of some high temperature inorganic salt compositions.

Compound	Composition	Melting point (°C)	Heat of fusion (kJ/kg)	References
$NaOH/NaCl/Na_2CO_3$	77.2/16.2/6.6	318	290	[30]
$LiCl/LiCrO_4/LiVO_3/LiF$	41.5/35.1/16.4/7.0	340	177	[31]
$LiCl/LiVO_3/LiF/Li_2SO_4/Li_2MoO_4$	42.0/17.4/16.2/11.6/11.6	363	284	[32]
$K_2CO_3/Na_2CO_3/Li_2CO_3$	34.5/33.4/32.1 a	397	276	[33,34]
$K2CO_3/Na_2CO_3/Li_2CO_3/$	35/33/32 a	397	276	[33,34]
$LiCl/LiF/Li_2SO_4/Li_2MoO_4$	51.5/16.2/16.2/16.2	402	291	[35]
LiOH/LiF	80/20	427	1163	[36]
$LiVO_3/LiF/Li_2MoO_4/Li_2SO_4$	43.8/25/16.5/14.8	428	260	[37]
LiF/LiOH	80/20	430	528	[38]
$NaCl/MgCl_2$	61.5/38.5 a	435	328	[17,53]
$LiF/KF/NaF/BaF_2$	45.7/41.2/11.3/1.8	438	332	[38]
LiF/KF/NaF/KCl	42.5–45.5/41.0–43.0/10.7–11.5/2.8–3.0	440–448	682–692	[54]
$KF/LiF/NaF/MgF_2$	55.1/27.1/11.9/5.9 a	449	699	[39]
KF/LiF/NaF	59.1/29.2/11.7 a	454	414	[39]
LiF/KF/NaF	46.5/42/11.5	454	325	[38]
KF/LiF/NaF	59/29/12 a	463	442	[40]
LiF/LiCl	73.6/26.4	485	403	[38]
KF/LiCl	50/50	487	344	[38]
K_2CO_3/Li_2CO_3	53/47 a	488	342	[33,34]
K_2CO_3/Li_2CO_3	53.4/46.6 a	488	391	[41]
KF/LiF	67/33 a	493	458	[40]
$LiVO_3/Li_2MoO_4/LiF$	53.0/29.0/18.0	493	297	[42]
Na_2CO_3/Li_2CO_3	56/44 a	496	370	[33,34]
K_2CO_3/Li_2CO_3	72/28 a	498	263	[33,34]
K_2CO_3/Li_2CO_3	71.5/28.5 a	498	316	[41]
Na_2CO_3/Li_2CO_3	55.7/44.3 a	498	393	[41]
K_2CO_3/Li_2CO_3	65/35 a	505	344	[33,34]
$Na_2MoO_4/NaBr/NaF$	55/43/2 a	506	241	[43]
ZrF_4/NaF	79.9/20.1 a	510	255	[39]
$K_2CO_3/KCl/NaF$	62/21/17 a	520	274	[33,34]
$KF/KCl/K_2CO_3$	23/40/37 a	528	283	[33,34]
$K_2CO_3/KCl/KF$	37/40/23 a	528	283	[33,34]
$LiF/NaF/CaF_2/BaMoO_4/BaF_2$	36.1/34/18.5/8.1/3.3	536	653	[44]
$Li_2SO_4/Li_2MoO_4/CaMoO_4$	59.8/36.7/3.5 a	538	406	[45]
$Na_2CO_3/Li_2CO_3/K_2CO_3$	60/20/20 a	550	283	[33,34]
$K_2CO_3/Li_2CO_3/Na_2CO_3/$	62/22/16 a	550	288	[33,34]
KBr/KF	60/40 a	576	315	[43]
KF/KCl	55/45	605	407	[43]
$NaF/LiF/CaF_2$	38.3/35.2/26.5	615	636	[39]
$LiF/NaF/CaF_2$	52/35/13	615	640	[36]
KBr/K_2MoO_4	65/35 a	625	90.5	[46]
$Li/NaF/MgF_2$	46/44/10	632	858	[36]
NaBr/NaF	73/27	642	360	[47]
LiF/NaF	60/40	652	816	[36]
$MgF_2/LiF/CaF_2/NaF$	37.25–37.6/34.51–34.79/24.5–25.0/3.21–3.31	651–657	460–470	[55]
NaCl/NaF	66.5/33.5	675	572	[47]
$Li_2SO_4/CaSO_4/CaMoO_4$	82/11.44/6.56 a	680	207	[43]
$LiF/NaF/MgF_2$	62/19/19	693	690	[48,49]
Na_2CO_3/K_2CO_3	52.2/47.8 a	710	176	[41]
K_2CO_3/Na_2CO_3	50/50 a	710	163	[41]
K_2CO_3/Na_2CO_3	51/49 a	710	163	[33,34]
LiF/MgF_2	70/30	728	520	[48,49]
$NaF/CaF_2/MgF_2$	65/23/12	743	568	[50]
LiF/MgF_2	67/33	746	947	[36]
$LiF/KF/MgF_2$	74/13/13	749	860	[48,49]
LiF/CeF_3	80/20	756	500	[48,49]
LiF/CaF_2	81.5/19.5	769	820	[48,49]
KF/CaF_2	85/15	780	440	[48,49]
KF/MgF_2	85/15	790	520	[48,49]
$NaF/MgF_2/KF$	64/20/16	804	650	[47,51]
$NaF/MgF_2/KF$	62.5/22.5/15	809	543	[36,50]
NaF/CaF_2	68/32	810	600	[48,49]
NaF/MgF_2	75/25	832	627	[36,50]
$CaF_2/CaSO_4/CaMoO_4$	49/41.4/9.6	943	237	[52]

a = (wt%).

temperatures, it has been the main material used for experimental fins. In Fig. 3 some typical fin configurations are shown.

For temperatures below 400 °C aluminum fins can be applied. It has been proven that there is no degradation of the material after testing more than 400 h with $NaNO_3$ as PCM [88]. Both, the aluminum and graphite sheets show no corrosion due to the contact with the galvanized steel of the pipes. Steel fins can be used; however, these fins occupy more volume than those made of graphite sheet to achieve the same performance in heat transfer, and therefore, the cost of steel fins is significantly higher.

Table 3
Thermophysical properties of some inorganic eutectic compositions with PCM potential.

Compound	Composition	Melting temperature (°C)	Heat of fusion (kJ/kg)	References
KOH/LiOH	60/40 a	314	341	[21]
$LiCl/KCl/BaCl_2$	54.2/39.4/6.4	320	170	[38]
KNO_3/KCl	96/4 a	320	150	[21]
$LiCl/KCl/LiCO_3/LiF$	47.4–47.7/46.8–47/3.2–3.4/2.1–2.4 a	340–343	375–380	[56]
$KNO_3/KBr/KC$	80/10/10 a	342	140	[21]
LiCl/NaCl/KCl	43/33/24 a	346	281	[21]
LiCl/KCl	58/42	348	170	[38]
$MnCl_2/KCl/NaCl$	45/28.7/26.3	350	215	[57]
$Li_2MoO_4/LiVO_3/LiCl/Li_2SO_4/LiF$	27.1–27.6/24.8–25.3/23.4–24.2/ 17.3–17.8/6.1–6.2 a	360–363	278–284	[30]
$LiCl/LiVO_3/LiF/Li_2SO_4/Li_2MO_4$	42.0/17.4/17.4/11.6/11.6	363	284	[32]
NaOH/NaC	80/20 a	370	370	[21]
$MgCl_2/KCl/NaCl$	60/20.4/19.6 a	380	400	[21]
$MgCl_2/NaCl/KCl$	57.0–53/22.5–26.5/18.5–22.5/a	385–393	405–410	[58]
$MgCl_2/NaCl/KCl$	45.4/33/21.6	385	284	[57]
$KCl/MnCl_2/NaCl$	45.5/34.5/20	390	230	[57]
$MgCl_2/NaCl/KCl$	50/30/20	396	291	[57]
$MgCl_2/NaCl/KCl$	51/27/22	396	290	[57]
$K_2CO_3/Na_2CO_3/Li_2CO_3$	34.5/33.4/32.1 a	397	276	[21]
$KCl/MnCl_2/NaCl$	37.7/37.3/25	400	235	[57]
$LiCl/LiF/Li_2SO_4/Li_2MoO_4$	51.5/16.2/16.2/16.2	402	291	[35]
$NaCl/MgCl_2$	56/44	430	320	[57]
$KCl/ZnCl_2$	54/46 a	432	218	[33,34]
$KCl/MgCl_2$	61/39 a	435	351	[33,34,59]
$NaCl/MgCl_2$	56.2/43.8	442	325	[57]
$LiCl/Li_2SO_4/Li_2MoO_4$	58.5/23.6/17.9	445	327	[60]
$MnCl_2/KCl$	64/36	448	236	[57]
$LiCl/LiVO_3/Li_2SO_4$	49.0/38.25/12.75	449	450	[61]
$MnCl_2/KCl$	65/35	450	237	[57]
$NaCl/MgCl_2$	60/40	450	328	[57]
$MgCl_2/NaCl$	52/48 a	450	430	[33,34,59]
$CaCl_2/NaCl/KCl/NaF$	47.6/41.3/8.1/2.9	460	231	[57]
$NaCl/CaCl_2/MgCl_2/KCl$	47.4/41.6/8.8/2.2	460	245	[57]
$CaCl_2/NaCl/KCl$	50/42.75/7.25	465	245	[57]
$MgCl_2/KCl$	64/36 a	470	388	[33,34,59]
$KCl/NaCl/MgCl_2/BaCl_2$	52.3/20.7/18.2/8.7	475	248	[57]
$KCl/NaCl/CaCl_2/BaCl_2$	47.3/22.7/16.9/13.1	478	208	[57]
$KCl/NaCl/CaCl_2/BaCl_2$	42.7/25.8/22.2/9.3	479	217	[57]
$LiCl/LiF/MgF_2$	69.5/26.5/4	484	157	[62]
$MgCl_2/CaCl_2/KCl$	48/27/25 a	487	342	[33,34,59]
$CaCl_2/NaF/CaF_2$	50/48.5/1.5	490	264	[57]
$CaCl_2/NaCl$	52.3–55/45–47.2	490–500	233–239	[57]
$CaCl_2/NaCl$	52.8/47.2	500	239	[57]
$CaCl_2/NaCl$	67/33 a	500	281	[33,34,59]
$CaCl_2/NaCl/KCl$	66/29/5 a	504	279	[33,34,59]
$SrCl_2/NaCl/KCl$	68/19/13 a	504	223	[33,34]
$K_2CO_3/KCl/NaF$	62/21/17 a	520	274	[33,34]
$Na_2MoO_4/NaBr/NaCl$	55/40/5	524	215	[43]
$KCl/K_2CO_3/KF$	40/37/23 a	528	283	[33,34]
$SrCl_2/MgCl_2$	63/37 a	535	239	[33,34]
$BaCl_2/KCl/NaCl/$	53/28/19 a	542	221	[33,34,59]
$BaCl_2/CaCl_2/KCl/$	47/29/24 a	551	219	[33,34,59]
$NaCl/NiCl_2$	52/48	573	558	[36]
$LiCl/MgF_2$	94.5/5.5	573	131	[62]
KF/KCl	55/45	605	407	[63]
$NaCl/Na_2MoO_4/NaBr$	38.5/38.5/23	612	168	[64]
$CaCl/CaSO_4/CaMoO_4$	38.5/11/4	673	224	[65]
$LiF/MgF_2/KF$	64/30/6	710	782	[21]
LiF/CaF_2	80.5/19.5	767	790	[21,66]

a=(wt%).

4.2. PCM embedded porous matrices

A porous matrix may be a metallic matrix or a matrix made of a naturally porous material such as graphite. Fiedler et al. [89] have found that copper matrices achieve approximately an increase of 80% in the effective thermal conductivity compared to aluminum matrices. It was found that a further increase is possible using diamond-coated copper matrices.

The effect of impregnating highly conductive porous matrices with PCM was investigated by Mesalhy et al. [90]; the results indicate that the performance improvement depends both on the porosity of the matrix and its conductivity. In pure PCMs, fusion rate was inferior in the lower portion of the container in comparison with the upper portion because the melting process is dominated by convection. With a porous matrix, the melting rate in the lower portion can be increased. It was found that the improvement due to the use of the porous structure is dependent on the porosity of the matrix. Low values of porosity lead to a higher effective thermal conductivity; therefore, there should be an increase in the performance enhancement. However, a decrease

Table 4
Thermophysical properties of some metallic alloys with PCM potential.

Compound	Composition (wt%)	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/m^3)	References
Zn/Mg	53.7/46.3	340	185	4600	[67]
Zn/Mg	52/48	340	180	n.a.	[68,69]
Zn/Al	96/4	381	138	6630	[67]
Al/Mg/Zn	59/33/6	443	310	2380	[68,69]
Al/Mg/Zn	60/34/6	450.3	329.1	n.a.	[41]
Mg/Cu/Zn	60/25/15	452	254	2800	[68,69]
Mg/Cu/Ca	52/25/23	453	184	2000	[68,69]
Al/Mg	65.35/34.65	497	285	2155	[67]
Al/Cu/Mg	60.8/33.2/6	506	365	3050	[67]
Al/Cu/Si/Mg	64.6/28/5.2/2.2	507	374	4400	[67]
Al/Cu/Mg/Zn	54/22/18/6	520	305	3140	[68,69]
Al/Cu/Si	68.5/26.5/5	525	364	2938	[67]
Al/Cu/Sb	64.3/34/1.7	545	331	4000	[67]
Al/Cu	66.92/33.08	548	372	3600	[67]
Al/Si/Mg	83.14/11.7/5.16	555	485	2500	[67]
Al/Si	87.76/12.24	557	498	2540	[67]
Cu/Al/Si	49.1/46.3/4.6	571	406	5560	[67]
Al/Cu/Si	65/30/5	571	422	2730	[68,69]
Al/Si/Sb	86.4/9.6/4.2	575	471	2700	[67]
Si/Al	86/12	576	560	2700	[70]
Si/Al	80/20	585	460	n.a.	[70]
Zn/Cu/Mg	49/45/6	703	176	8670	[68,69]
Cu/P	91/9	715	134	5600	[68,69]
Cu/Zn/P	69/17/14	720	368	7000	[68,69]
Cu/Zn/Si	74/19/7	765	125	7170	[68,69]
Cu/Si/Mg	56/27/17	770	420	4150	[68,69]
Mg/Ca	84/16	790	272	1380	[68,69]
Mg/Si/Zn	47/38/15	800	314	n.a.	[68,69]
Cu/Si	80/20	803	197	6600	[68,69]
Cu/P/Si	83/10/7	840	92	6880	[68,69]
Si/Mg/Ca	49/30/21	865	305	2250	[68,69]
Si/Mg	56/44	946	757	1900	[68,69]

Table 5
Thermophysical properties of some metallic eutectic alloys.

Compound	Composition (wt%)	Melting temperature (°C)	Heat of fusion (kJ/kg)	References
Zn/Mg	53.7/46.3	340	185	[22]
Zn/Al	96/4	381	138	[22]
Al/Si/Sb	86.4/9.4/4.2	471	471	[22]
Al/Mg	65.35/34.65	497	285	[22]
Al/Cu/Mg	60.8/33.2/6.0	506	365	[22]
Al/Mg/Si/Cu	64.1/28/5.2/2.2	507	374	[22]
Al/Cu/Si	68.5/26.5/5.0	525	364	[22]
Al/Cu/Sb	64.3/34/1.7	545	331	[22]
Al/Cu	66.92/33.08	548	372	[22]
Al/Si/Mg	83.14/11.7/5.16	555	485	[22]
Al/Si	87.76/12.24	557	498	[22]
Cu/Al/Si	49.1/46.3/4.6	571	406	[22]

in the porosity results in a decrease in the enhancement effect because the low porosity of the matrix dampens the movement of the liquid PCM and the natural convection.

Krishnan et al. [91] obtained similar results through a numerical study of the melting process in a rectangular container filled with metal foam impregnated with PCM. It can be concluded then that the porous matrix should not only possess high thermal conductivity but high porosity as well to obtain the highest possible performance enhancement.

Recently graphite has been extensively studied as a heat transfer material due to its high thermal conductivity, high melting point, low density and chemical resistance [77,92–95]. Expanded graphite (EG) is an interesting alternative due to its high porosity which means high absorbability. When the EG is mixed with a PCM, the molten PCM is absorbed into the pores of the EG resulting in a composite PCM. The thermal conductivity and heat capacity of the PCM composite depend on the proportion of graphite and PCM.

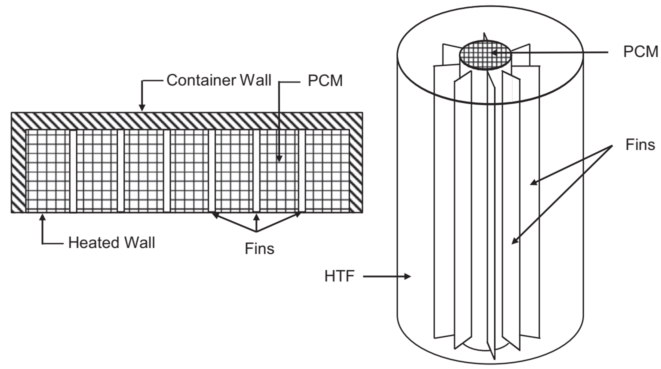


Fig. 3. Common fin arrangements.

The use of graphite to improve the thermal conductivity of the PCM is not limited to low melting point PCMs such as organic compounds; it has also been proposed for PCM with high melting points such as saline compounds and eutectic mixtures [95,96].

Generally, PCM–graphite composites are made by mixing graphite with the molten PCM. This same approach was adopted by Pincemin et al. [96] to prepare a eutectic salt–graphite composite. Due to the high viscosity of the salt and the similarity between the salt and graphite densities, graphite particles could be well dispersed in the molten salt and an isotropic compound was obtained. However, this method was costly because the high melting point PCM required more energy, and there were some limitations due to corrosion on the equipment and safety issues. The authors resorted to a cold compression method, in which after the solid PCM has been mixed with the graphite powder, the mixture is compressed at room temperature. Compression eliminates most of the porosity resulting in a monolithic composite with anisotropic properties. Pincemin et al. [95] used different particle size graphite powders for preparing the composite. Thermal conductivity is dependent not only on the amount of graphite but also on the particle size. Based on these results, it is suggested that for a greater percentage of graphite in the mixture a larger particle size should be employed. In regard to storage capacity, smaller particles have a larger capacity as the amount of graphite is increased. The results also show that the composite has a nearly congruent melting point, which is an advantage as it would result in a nearly isothermal operation. However, cold compressed compounds are not always reliable since the smallest presence of impurities or mechanical stresses leads to salt leakage.

4.3. Dispersion of highly conductive particles within the PCM

Using PCM compounds with graphite is a form that has proven to be efficient and successful for performance improvement in LHS systems. Either way, the PCM–graphite composites can only be prepared through various chemical and mechanical processes such as thermal treatment, drying, blending, grinding and compression, etc., processes that are time and energy consuming.

Elgafy and Lafdi [97] have reported, as has been already mentioned, that the porosity of the graphite is critical in the effectiveness of the compounds. When using graphite pores of small size, there may be a decrease in the amount of latent heat, because the small pores hinder molecular movement and it is very difficult to impregnate the porous medium with the PCM. Moreover, increasing the pore size reduces the capillary force resulting

in leakage of the liquid PCM. The dispersion of highly conductive particles in the PCM technique is much simpler for increasing the thermal conductivity of the PCM, since the highly conductive metal particles are free from the disadvantages mentioned above.

Metawee and Assassa [98] conducted experiments to investigate the improvement due to the dispersion of microparticles of aluminum in the performance of a solar collector based on PCM. As a result of the increased thermal conductivity, the load time decreased by 60% compared with the charging time of pure PCM; during the discharge the effect is more pronounced and a more homogeneous process is observed. To evaluate the overall benefit of embedding aluminum particles, the average efficiency was calculated daily. The results showed a significant increase. For all mass flow rates of water, the highest daily average was 94% obtained with the PCM composite while with pure PCM it was only 55%; although this method was proved in low temperature water heating system, it could be applied for high temperature applications as well. Despite the improvement in performance due to the addition of particles, the effect on the storage capacity of the PCM is not reported.

4.4. Multiple PCM method

Using multiple PCMs in a LHS system has been reported in the literature as another attractive technique for performance improvement. Employing multiple PCMs means that the LHS unit contains more than one PCM with different melting temperatures. The heat transfer rate in the unit and thus LHS system performance during charging (fusion) and discharge (solidification) depends primarily on the difference between the temperature of the HTF and the PCM melting point [76].

If a single PCM is used, this temperature difference obviously would decrease in the flow direction of the HTF. This results in a decreased heat transfer rate and therefore poor performance of the unit. If multiple PCMs with different melting temperatures are packaged in the unit in decreasing order by their melting points, then there will be an almost constant temperature difference during the melting process, even if the HTF temperature decreases. This leads to a nearly constant heat flow to the PCM. During discharge, if the HTF flow direction is reversed, the PCMs remain in the increasing order of their melting points, and again almost constant heat flow is possible from the PCM to the HTF. The usage of multiple PCMs in a shell and tube unit is illustrated in Fig. 4.

A great amount of work has been devoted to investigating this technique. Farid and Kanzawa [99] used three PCMs with different melting points contained in cylindrical capsules. Air was used as HTF. During loading and unloading a 10% increase in heat transfer rate was obtained. An experimental study of Michels and Pitz-Paal [100] has shown the benefit of using multiple PCMs in a shell and tube module. The shell was loaded with three PCMs and synthetic oil flowed through the inner tube. It was noted in this case that a larger portion of PCM experienced phase change during the cycle. Therefore, in a period of time, the PCM unit three has a higher fraction of phase change and a greater storage capacity compared to a single PCM unit. In the above configurations, the HTF flows through the system and therefore all PCMs accommodated in the flow direction (axial direction) are in contact with the HTF. In this case, since the LHS is surrounded by HTF, there is no axial variation in temperature within the HTF. In such a configuration, multiple PCMs must be accommodated radially instead of axially to extract maximum benefit. As the PCM located in the center of the one PCM unit has minimum thermal contact with the HTF, fusion cannot be expected immediately. With multiple PCMs it is possible to have the material with the lowest melting point in the center and other PCMs arranged in ascending order from the center of the unit to the outside. In this way a fusion, more or less simultaneous at all points can be achieved since an almost constant temperature difference in the radial direction can be kept.

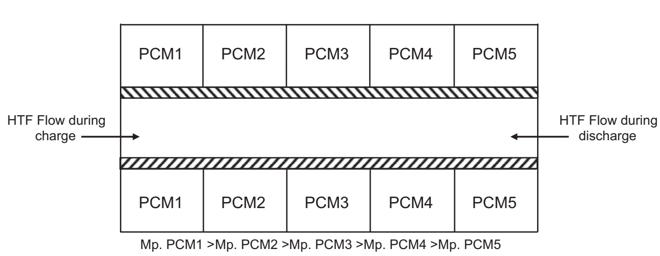


Fig. 4. Multiple PCMs on a shell and tube unit.

When multiple PCMs are used to improve the performance of a LHS system, it is important to choose the right combination. This corresponds to an appropriate difference between the melting points and relative proportions of the PCM. Fang and Chen [101] performed a numerical study in a shell and tube module to examine the effect of different combinations of PCM. The study is limited to the three PCM models, and conclusions can be extended to models of five or more PCMs. The results indicate that higher melting fractions and therefore higher amounts of storage are achieved for bigger differences in melting point with the same amount of PCM central (used in the one PCM module). An Increase in the fraction melting and energy storage was observed in all cases when the core PCM ratio decreased. This is because a decrease in the proportion of core PCM leads to an increase in the proportion of PCM with lower melting point, which takes less time to melt. However, in all cases there was an optimal value for the ratio of central PCM to achieve high melting fraction/energy storage. The results showed that the optimum core PCM proportion increases with an increase in the melting point difference between the PCMs.

Although using multiple PCMs seems an attractive technique to improve the thermal performance of a conventional LHS system, using multiple PCM in combination with finned surfaces would be a better enhancement technique as fins provide different compartments for storing PCM [102]. Most studies using multiple PCMs have been performed with arbitrarily selected materials, and it is clear that in this method the selection of an appropriate combination of PCM is crucial to produce the greatest improvement in performance; this shows that more studies are needed to investigate in depth the best combinations.

5. Applications in power generation

TES has always been associated closely with solar installations because solar energy availability is limited, and does not coincide with energy demand periods. Nowadays there are several solar power generation plants that have TES systems within their facilities, for example, Andasol I–III in Guadix Spain, PS10 and PS20 in Seville, Spain and Solar I and II in California USA. All these solar plants make use of different storage media and HTFs; however none of them utilizes latent heat as their storage method regardless of the advantages, mainly due to the previously discussed PCM downsides.

To address the shortcomings of the current solar thermal energy power generation technologies and establish the usage of LHS as primary storage mechanism in solar power plants, several proposals have been developed.

One of the proposals is a storage system with a cascade LHS (CLHS) configuration, shown in Fig. 5. In this case, different PCMs were tested in different storage modules. A theoretical analysis of

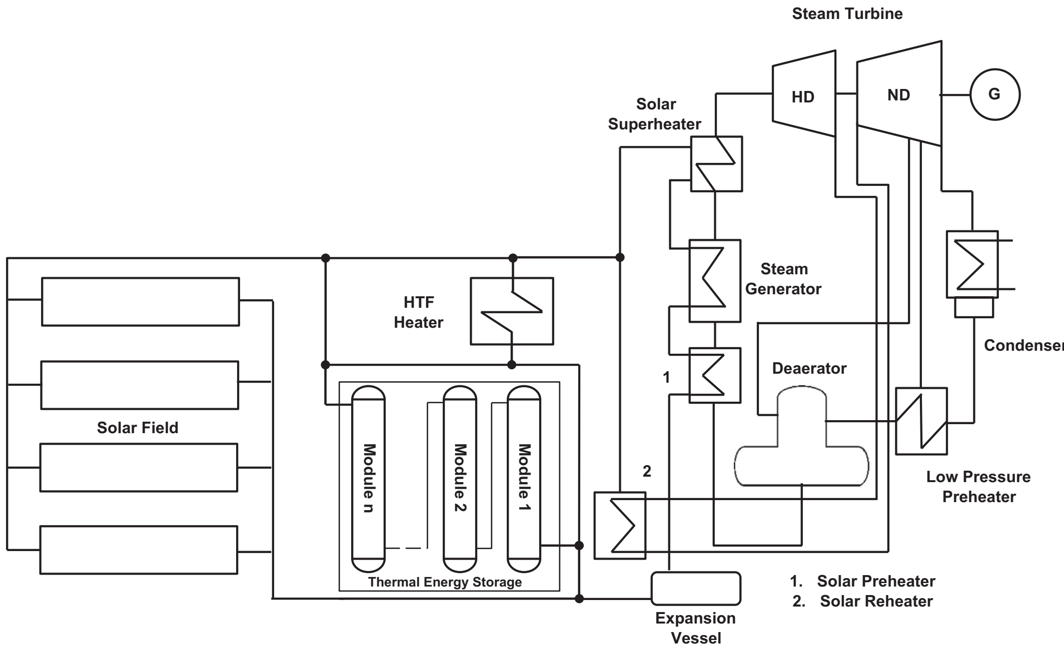


Fig. 5. Scheme of installation of a parabolic through plant, with PCM storage.

a simplified model of this new plant [103] showed that for a simple process of loading/unloading the Cascade LHS (CLHS) has a number of advantages if operated in counter flow. A study states the positive effect of a CHLS compared with a conventional LHS, with respect to a further use of the possible phase change, and more uniform outlet temperature over a period of time [100]. This TES concept was designed for solar plants with parabolic trough technology in their solar fields, but with the correct choice of PCM the technology can be transferred to central tower plants.

If a comparison is made between CLHS and a two tank molten salt system, the findings [100] are as follows:

- Using less salt, CLHS has the same storage capacity as the two tank system.
- A heat exchanger is needed with CLHS, but a more uniform outlet temperature is obtained.
- The two tank system requires two additional pumps for the salts, and additional heat to maintain the salt in liquid state, which the CLHS does not require.

Although the technical feasibility of the CLHS system has been tested, the further development of the concept is hampered by the complexity of the system and the uncertainty over the lifetime of the PCM.

Another energy storage proposal for solar plants, made by the German aerospace center (DRL) together with the German center for solar energy and hydrogen research (ZSW), is a combination of sensible and latent heat storage [104]. Fig. 6 shows a diagram of the system.

The prototype of this hybrid storage system, built in DLR Stuttgart, had a capacity of 200 MWh and was designed for a 3 h charge time and a 1 h discharge period. The fluid used was synthetic oil and three different storage materials were used: $NaNO_3$, concrete, and a mixture of NaOH and NaCl. The most innovative aspect of this concept was the possibility of increasing the efficiency of the systems, due to the combination of the good thermal conductivity and reduced cost of concrete with the good storage characteristics of the PCM [105].

The DLR is working on concepts for reducing the specific resistance to heat conduction in the PCM and the average distance

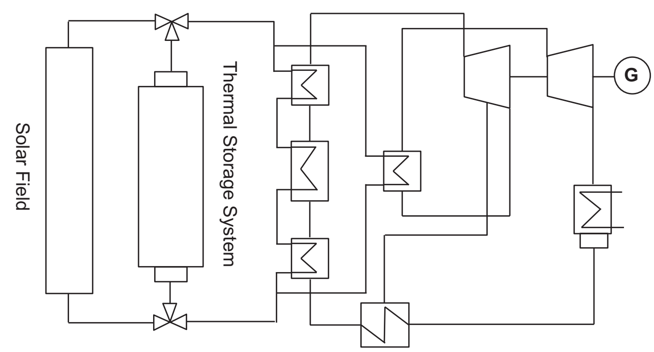


Fig. 6. Scheme of the solar energy storage system proposed by DLR–ZSW.

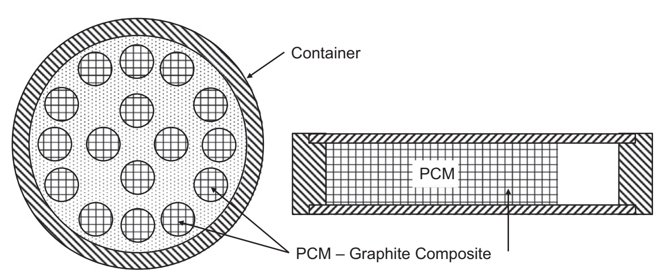


Fig. 7. Internal arrangement of PCM–graphite composite.

for heat conduction within the storage material. The first approach consists of an internal arrangement, where the HTF flows along a container and through capsules of a PCM–graphite composite, as shown in Fig. 7.

In this case, the container is pressurized and a high rate of material encapsulation can be achieved. The arrangement may also be external, as shown in Fig. 8, which is characterized by low pressure storage, and from a manufacturing process point of view, low manufacturing complexity of the material.

The high cost of graphite sheets is compensated by its low density and high thermal conductivity; besides, the investment costs of extended structures of graphite for heat transfer are lower than those of steel. Another advantage of the graphite foil is its

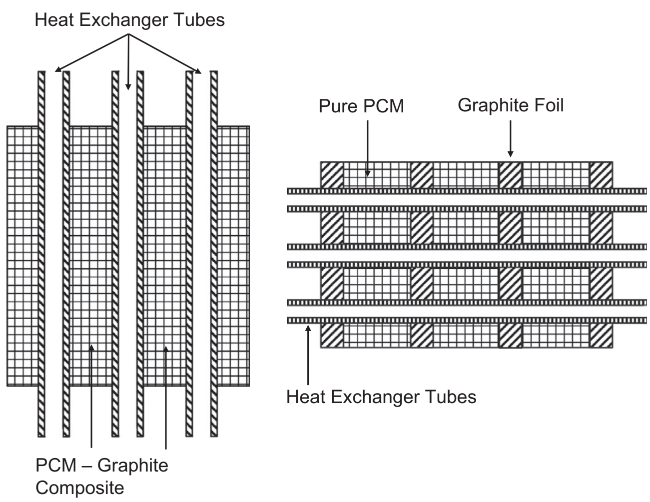


Fig. 8. External arrangement of PCM–graphite composite.

good corrosion resistance against nitrate salts, which are common high temperature PCMs and whose corrosive behavior precludes the use of aluminum, which otherwise would be attractive for its high thermal conductivity and low density.

All these concepts can be applied in solar thermal plants with a power range of 10–300 MW, and operation temperature ranges between 250 °C and 350 °C.

6. Conclusions

This paper reviews thermal energy storage information available in the literature with a special focus on high temperature latent heat storage, aiming to provide the reader with a broad overview of the design considerations that must be taken and technical challenges when working with LHS systems. It discusses several different heat transfer and performance enhancement techniques employed by researches and reviews a series of high temperature PCMs seeking to assist developers in the material selection being a comprehensive thermophysical properties database. The following concluding remarks can be mentioned:

- Thermal energy storage through latent heat offers great advantages such as high energy density, far superior than that of sensible heat storage and an almost isothermal operation, making it a very promising technology for the future.
- Despite the proven benefits of LHS, in current solar power plants only sensible heat storage systems are being used, mainly because there are some drawbacks of the PCM usage that still need to be addressed; however, the development of more efficient and cost-effective TES systems is vital for the improvement and growth of solar power plants.
- High temperature materials with melting temperatures above 300 °C, proposed and analyzed by various authors as possible PCMs, are reviewed. Among them pure inorganic salts, saline compounds, salt eutectic, metal and metallic eutectic alloys are found. Most of the salt compounds are chloride, fluoride or nitrate based.
- The major drawback of salts (and many other low temperature PCMs) is their low heat conductivity, which has held back the widespread utilization of LHS systems. This paper reviews different techniques for improving heat transfer and performance which include using extended surfaces, the multiple PCM method, high conductivity particle dispersion and porous matrices embedded with PCM. This review is intended to provide an overview of the features, limitations and obtained results of each enhancement method to promote further research.
- The use of metal alloys as phase change materials has been underestimated by researchers although they have desirable properties such as high thermal conductivity, low corrosivity, small volume change associated with phase change and no subcooling, thanks to which for certain applications, especially when weight is not a decisive factor, they are able to compete with salts.
- Many authors point out that there are major discrepancies between the data of melting temperature, latent heat of fusion, thermal conductivity and density in both solid and liquid, for the same PCM in the literature. The inconsistency is largely due to the lack of international standard methods for PCM testing. Furthermore, practically all experiments have been limited only to temperature and latent heat of fusion measurements and so information regarding the temperature dependence of certain parameters such as thermal conductivity or density is rather scarce.

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